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Catalysts for Low-Temperature Decomposition of VOCs

**S.E. Roark, J.H. White, O. Bull
A.F. Sammells, J.D. Wander**

**Eltron Research
4600 Nautilus Court South
Boulder, Colorado 80301-8241**

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**AIR FORCE RESEARCH LABORATORY
MATERIALS & MANUFACTURING DIRECTORATE
AIR EXPEDITIONARY FORCES TECHNOLOGIES DIVISION
139 BARNES DRIVE, STE 2
TYNDALL AFB FL 32403-5323**

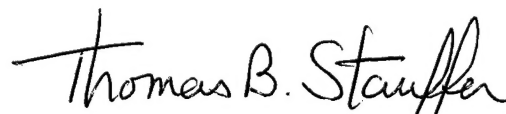
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JOSEPH D. WANDER, Ph.D
Program Manager



THOMAS B. STAUFFER, Ph.D, DR-IV, DAF
Chief, Weapons Systems Logistics Branch



RANDY L. GROSS, Col, USAF, BSC
Chief, Air Expeditionary Forces Technologies Division

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13. ABSTRACT (Maximum 200 words) Eltron Research, Inc., is currently developing multicomponent metal-oxide and supported noble-metal catalysts for the destruction of volatile organic compounds (VOCs) in air at low temperatures. The goal for this work is to produce a simple, cost-effective technology for reducing the concentration of VOCs in air to acceptable levels before the air is released into the atmosphere or recirculated. Specific application areas include ventilated work spaces for spray painting and engine maintenance (degreasing and fuel line repair), indoor air decontamination, dry cleaning, food processing (grills and deep fat fryers), fume hoods, residential use, and solvent-intensive industrial processes. The components of the catalysts were chosen based on their anticipated oxygen surface mobility, resistance to poisoning, multiple oxidations states, and documented activity for oxidation reactions. Catalysts were screened with and without dispersed platinum for conversion of 1-butanol, toluene, and methyl ethyl ketone (MEK) into carbon dioxide and water. The concentrations of VOCs in the feedstream were maintained at ~100 ppm, and the space velocity was between ~1,000 and 26,000 hr ⁻¹ . Catalysts with the best overall performance in the absence of noble metals generated complete conversion of 1-butanol into CO ₂ at 150 °C, 47% conversion at 100 °C, and 15% conversion at 80 °C. For toluene these catalysts generated complete conversion at 200 °C, and conversions as high as 75% at 150 °C. Adding Platinum to these materials further improved low-temperature activity and routinely allowed greater than 50% conversion of VOCs to CO ₂ at temperatures of 100 °C and lower. Although it was generally found that catalyst destruction decreased in the order 1-butanol>MEK>toluene, some of the most-active materials demonstrated different trends, as well as large disparities in activity for these VOCs.				
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Catalysts for Low-Temperature Decomposition of VOCs

Shane E. Roark, James H. White, Jason W. Keeley, Ozlem Bull, Anthony F. Sammells
Eltron Research, Inc.
4600 Nautilus Court South
Boulder, CO 80301
www.eltronresearch.com

Joseph D. Wander
Air Force Research Laboratory
AFRL/MLQE
139 Barnes Dr., Ste. 2
Tyndall AFB, FL 32403-5323

ABSTRACT

Eltron Research, Inc. is currently developing multi-component metal oxide and supported noble metal catalysts for the destruction of volatile organic compounds (VOCs) in air at low temperatures. The goal for this work is to produce a simple, cost-effective technology for reducing the concentration of VOCs in air to acceptable levels before the air is released into the atmosphere or re-circulated. Specific application areas include ventilated work spaces for spray painting and engine maintenance (degreasing and fuel line repair), indoor air decontamination, dry cleaning, food processing (grills and deep fryers), fume hoods, residential use, and solvent-intensive industrial processes.

The components of the catalysts were chosen based on their anticipated oxygen surface mobility, resistance to poisoning, multiple oxidation states, and documented activity for oxidation reactions. Catalysts were screened both with and without dispersed platinum for conversion of 1-butanol, toluene, and methyl ethyl ketone (MEK) to carbon dioxide and water. The concentrations of VOCs in the feedstream were maintained at ~100 ppm, and the space velocity was between ~1,000 and 26,000 hr⁻¹.

Catalysts with the best overall performance in the absence of noble metals generated complete conversion of 1-butanol to CO₂ at 150°C, 47% conversion at 100°C, and 15% conversion at 80°C. For toluene, these catalysts generated complete conversion at 200°C, and as high as 75% conversion at 150°C. Adding platinum to these materials further improved low-temperature activity and routinely enabled greater than 50% conversion of VOCs to CO₂ at temperatures of 100°C and lower. Although generally it was found that catalytic destruction decreased in the order of 1-butanol > MEK > toluene, some of the most active materials demonstrated different trends, as well as large disparities in activity for these VOCs.

INTRODUCTION

Increasing concern over detrimental environmental and health effects resulting from emission of volatile organic compounds (VOCs) has led to stricter emission regulation standards, and has fueled efforts to identify efficient and economical methods for VOC abatement. Conventional non-catalytic methods for removing VOCs from gaseous waste streams include

incineration¹ and carbon adsorption.² While both of these methods are effective, they either require special equipment and high temperatures, or secondary processing steps that are expensive to implement and maintain. Conversely, catalytic destruction of VOCs offers a less complicated and more economical and efficient emission control system than incineration or adsorption. Catalytic destruction occurs at much lower temperatures than incineration, and the reactors are simpler and cheaper to construct and operate. Furthermore, unlike adsorption methods, catalytic destruction is a one-step process for complete combustion of VOCs.

Traditionally, catalysts employed for destruction of VOCs are either metal oxides, or noble metals supported on relatively inactive materials such as Al_2O_3 or SiO_2 .³ While noble metal catalysts have higher overall activity for VOC destruction, metal oxides are much cheaper and have greater resistance to poisoning by feedstream components. As with noble metal catalysts, metal oxides also are active for combustion of VOCs with a range of organic functional groups.³⁻

¹⁰ For example, the oxides of Fe, Mn, Mg, Ni, Co, V, Zn, Ti, Mo, Cr, and Cu have been used for the combustion of alcohols, aldehydes, alkanes, olefins, methane, and carbon monoxide at temperatures between 250°C and 450°C.³ Similarly, numerous catalysts based on CeO_2 have recently been reported for VOC destruction.¹¹⁻¹⁵ Dispersion of noble metals such as Pt or Pd onto metal oxides can reduce the catalytic combustion temperature to a range between 100°C and 200°C, depending on the specific catalyst system and VOC. However, even with noble metal catalysts, the temperatures required to attain high activity generally are well above 100°C, and a significant reduction in operating cost could be realized by achieving catalytic combustion at near-ambient temperatures.

Considerable effort in the development of low temperature oxidation catalysts has been directed towards the oxidation of CO. In the early 1980's, Stark *et al.* demonstrated that Pt/SnO_x was very active for CO oxidation,¹⁶ and Hoflund *et al.* compared this catalyst to Au/MnO_x .¹⁷ The authors found that the Au/MnO_x system was more active than Pt/SnO_x and produced nearly 60% conversion of CO to CO_2 at only 35°C.¹⁷ Major advancements were achieved by Haruta *et al.* who demonstrated activity for the oxidation of CO below 0°C using highly dispersed Au on the oxides of Fe, Co, and Ni.^{18,19} Since Au alone is inactive towards oxidation, and the metal oxides are only active for CO oxidation at elevated temperatures, the results obtained by Hoflund *et al.* and Haruta *et al.* underscore the synergistic relationship between the noble metal and metal oxide support. It is anticipated that optimizing this synergy will be critical for achieving near-ambient activity for VOC oxidation.

The objective of the work described in this manuscript is to develop multi-component metal oxide and supported noble metal catalysts to further reduce catalytic combustion temperatures of VOCs. The performance of several proprietary catalysts with and without Pt for complete destruction of representative VOCs will be presented. It is anticipated that these catalysts under development will be used to produce a simple, cost-effective technology for reducing the concentration of VOCs in air to acceptable levels before the air is released into the atmosphere or re-circulated. Specific application areas include ventilated work spaces for spray painting and engine maintenance (degreasing and fuel line repair), indoor air decontamination, dry cleaning, food processing (grills and deep fryers), fume hoods, effluents from air stripping towers, wet-air oxidation, and solvent-intensive industrial processes.

EXPERIMENTAL

A. Catalyst Preparation

Proprietary catalysts were prepared and tested as powders with BET surface areas between 40 and 200 m²/g. The multi-component metal oxide catalysts (MMO) typically were synthesized by coprecipitation from appropriate mixtures of metal nitrates, followed by calcining in air at temperatures between 400°C and 600°C. Supported-Pt catalysts were prepared by incipient wetness/impregnation of the MMO powders. Supported-Pt catalysts were reduced at 300°C to 700°C for 3 to 4 hours under hydrogen prior to testing.

B. Catalyst Screening

Figure 1 shows a schematic diagram of the apparatus used for catalyst screening. The apparatus incorporated four reactors, each consisting of a furnace surrounding a 4-mm i.d. quartz tube containing the catalyst sample. VOCs were introduced into the reactors from cylinders of 200 ppm VOC/air mixtures (AirGas). The concentrations were adjusted to ~100 ppm by mixing the VOC supply with a second air line. Flow rates and mixing ratios were controlled by needle valves and monitored using both ball-type and bubble flow meters. Reactor temperatures were measured and adjusted using controllers paired with thermocouples inserted in the quartz reactor tubes to a height touching the top of the catalyst bed.

Prior to screening, catalyst samples were heated in line at 200°C overnight under a flow of air. Approximately 0.2 g of catalyst was used for each evaluation, which resulted in a 1-cm deep catalyst bed in the quartz reactor tubes. Based on the catalyst volume, VOC flow rates were adjusted to between ~3 and 70 ml/min to achieve space velocities (SV) between ~1,000 and 30,000 hr⁻¹. Representative VOCs used in this work were toluene, methyl ethyl ketone (MEK), and 1-butanol. These VOCs were chosen based on their use in spray paints and general popularity as solvents. Additionally, these VOCs represent a range of functionality, *i.e.* aromatic, ketone, and alcohol. Measurements

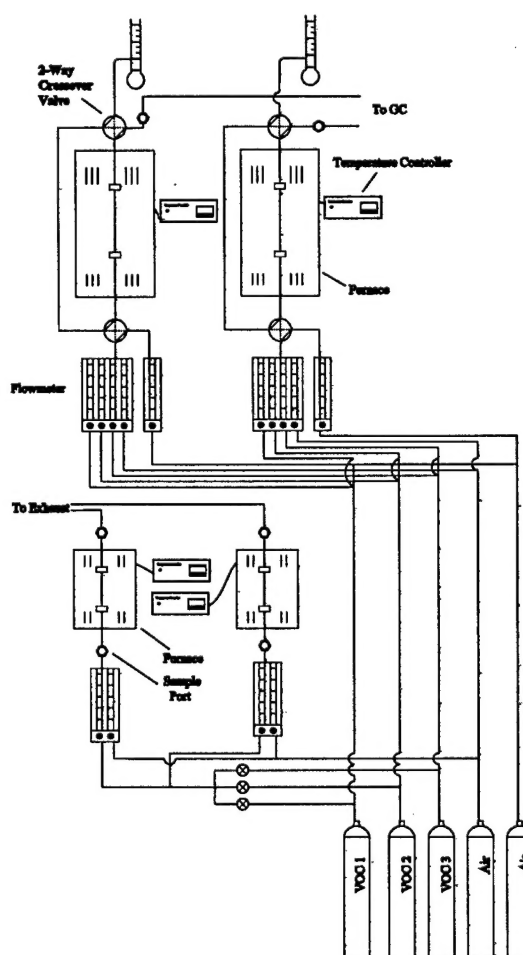


Figure 1. Schematic diagram of apparatus used for catalyst evaluation.

of the inlet VOC concentration and outlet VOC and CO₂ concentrations were accomplished by sampling through ports located on opposite sides of the reactors. Inlet and outlet VOC concentrations were determined from chromatograph peak areas using a Shimadzu GC-14A with flame ionization detection (FID) and a 1% AT 1000 Graphpac 60/80 column (Alltech). Product CO₂ concentrations were determined using a Hewlett-Packard 5890 GC with thermal conductivity detection (TCD) and a CTR-1 column (Alltech).

RESULTS AND DISCUSSION

A. Metal Oxide Catalysts

A summary of catalytic activity for conversion of 1-butanol to CO₂ is shown in Figure 2 for several materials at 80°C, 100°C, and 150°C. The concentration of 1-butanol was ~100 ppm in air, and the space velocity was ~6,000 hr⁻¹. Eltron proprietary catalysts shown in the figure were multi-component metal oxides

(MMO) absent of noble metals, and are indicated as MMO1, MMO2, MMO3, and MMO4. These materials were doped analogs of the single component metal oxide, MO1, also shown in the figure. For comparison, screening results for a commercial 1%Pt/Al₂O₃ catalyst (Alfa Aesar, surface area 300 m²/g) was included as well. The conversion values shown in the figure are averages of steady-state

measurements taken after approximately 10 to 24 hours at each temperature. Comparing the data at 150°C, the MMO catalysts all generated 100% conversion, whereas the unmodified MO1 catalyst generated 50% conversion. Moreover, the

conversion value for MMO1 at 100°C (47%) is approximately equal to the value for MO1 at 150°C. Since the MMO catalysts contain between 45% and 80% MO1 (% mole fraction of the metal component), and the crystallographic phase of MO1 is retained after modification with selected dopants, these results indicate that significant improvements in catalyst activity can be achieved through relatively minor modifications in catalyst composition. Comparison of the MMO catalysts to 1%Pt/Al₂O₃ demonstrates that all the MMO catalysts performed better than 1%Pt/Al₂O₃ at 150°C, and both MMO1 and MMO2 had better performance at 100°C.

Figure 3 contains a plot of percent conversion of 1-butanol to CO₂ versus time for MMO1 at several temperatures over a 56-hour test period. Steady-state activity decreased linearly from 150°C to 80°C. After reducing the test temperature from 200°C to 150°C, and from 150°C to 100°C, there was an induction period before steady-state activity was reestablished. This

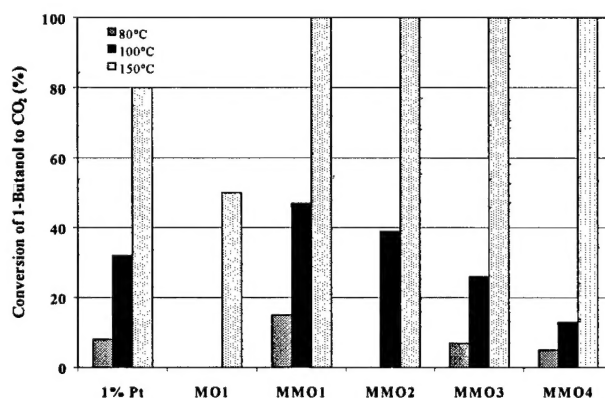


Figure 2. Summary of activity for conversion of 1-butanol to CO₂ at 80°C, 100°C, and 150°C. The 1% Pt catalyst (supported on Al₂O₃) is included for comparison. MO1 indicates a single-component metal oxide, and MMO1 through MMO4 indicate multi-component metal oxides derived from MO1. The 1-butanol concentration was ~100 ppm in air and the space velocity was ~6,000 hr⁻¹.

induction period lasted about 3 hours at 150°C and 6 hours at 100°C. Although not present in this data set, such an induction period generally is even longer at 80°C, and can last between 10 to 24 hours. This behavior is characteristic of high-surface-area catalysts when the VOC concentration is low, and is likely the result of VOC adsorption on the catalyst surface.²³ During the induction period, only product CO₂ is observed in the reactor effluent and there is a large disparity in the carbon balance between the inlet VOC concentration and reactor outlet. After steady-state activity was established, the catalyst demonstrated stable performance over the 7 to 20 hour test period, although there was a slight decrease in activity over time at 80°C.

Figure 4 shows a catalyst performance summary for conversion of toluene to CO₂. Toluene generally is more difficult to oxidize than 1-butanol, therefore, screening was performed at higher temperatures. In this figure, the single-component metal oxide MO1 again is shown, as well as four alternative multi-component compositions MMO5, MMO6, MMO7, and MMO8. As above, the VOC concentration was ~100 ppm in air and the space velocity was ~6,000 hr⁻¹. All of the MMO catalysts in the figure generated 100% destruction of toluene at 200°C, and the single-component oxide from which they were derived generated 89% conversion. However, reducing the temperature to 150°C resulted in a dramatic reduction in activity for all materials except for MMO5, which maintained 75% conversion of toluene to CO₂. Despite the drop in activity for the other materials, MMO6 still performed well with 50% conversion, and MMO7 and MMO8 had stable performance at greater than 20% conversion.

The data presented in the above figures represent the best results to date at Eltron using catalysts without noble metals for destruction of 1-butanol and toluene, and similar results also have been obtained for MEK. Considering all catalyst compositions tested at Eltron

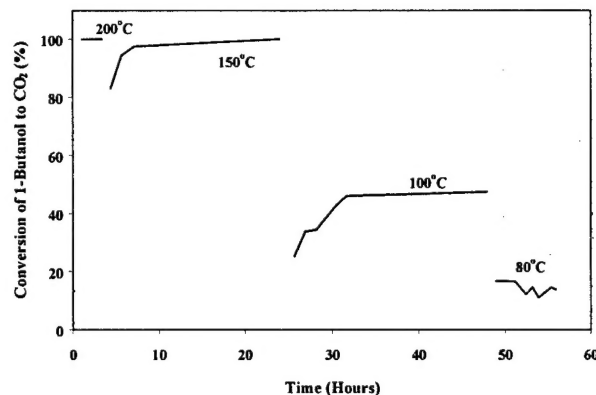


Figure 3. Plot showing conversion of 1-butanol to CO₂ as a function of time at 200°C, 150°C, 100°C, and 80°C using the Pt-free MMO1 catalyst. The 1-butanol concentration was ~100 ppm in air, and the space velocity was ~6,000 hr⁻¹.

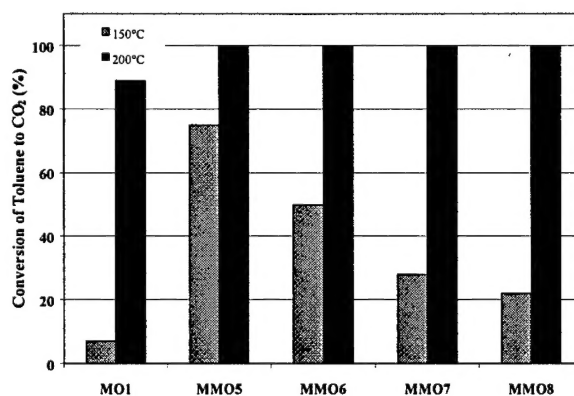


Figure 4. Summary of activity for complete conversion of toluene to CO₂ at 150°C and 200°C. MO1 indicates a single-component metal oxide, and MMO5 through MMO8 indicate multi-component metal oxides derived from MO1. The toluene concentration was ~100 ppm in air and the space velocity was ~6,000 hr⁻¹.

for destruction of these three VOCs, the very lowest temperatures producing high conversion have been observed for 1-butanol. However, the order of activity for destruction of these three VOCs changes with different compositions. In fact, the compositions with the best performance for 1-butanol destruction are not the same as those for toluene destruction. Based on these results it is apparent that treating effluents containing mixtures of VOCs will require a compromise in catalyst composition and activity, or compositions will be selected based on a target VOC in the mixture.

Table 1 summarizes the effect of space velocity on the activity of MMO1 for conversion of 1-butanol, MEK, and toluene to CO₂. For this composition, activity for complete VOC combustion decreased in the order of 1-butanol > MEK > toluene, as has been generally observed in the literature based on bond dissociation energies of the weakest C-H bond.²⁰⁻²² Although activity of these materials is not highly dependent on space velocity between about 1,000 and 6,000 hr⁻¹, these results demonstrate a significant drop in activity at space velocities above about 15,000 hr⁻¹. Despite this drop in activity, substantial conversion rates still are achieved at space velocities as high as 26,000 hr⁻¹.

Table 1. Summary of conversion of VOCs to CO₂ at 150°C as a function of space velocity for MMO1.*

VOC	Space Velocity (hr ⁻¹)	Conversion (%)
1-Butanol	6,000	97
	26,000	43
MEK	6,000	81
	17,000	33
Toluene	6,000	52
	15,000	18

*VOC concentration was approximately 100 ppm in air.

B. Supported Pt Catalysts

Figure 5 contains a summary of activity for conversion of 1-butanol to CO₂ using 5% Pt supported on the multi-component metal oxides MMO1 and MMO2 under the exact same conditions as in Figure 2. Not surprisingly, comparing the data in Figures 2 and 5 indicates a significant improvement in catalytic activity at lower temperatures upon adding Pt to the composition. For MMO1, Pt increased conversion at 80°C from 15% to 35%, and at 100°C from 47% to 66%. However, the highest activity for 1-butanol destruction observed to date at Eltron has been for 5%Pt on the unmodified single-component metal oxide MO1. Although the testing conditions were performed at a lower space velocity (*i.e.* 1,000 hr⁻¹ instead of 6,000 hr⁻¹), after a 20-hour induction period the 5%Pt/MO1 catalyst generated 95% conversion of 1-butanol to CO₂ at only 60°C. This result highlights the fact that the most active metal oxide catalysts are not necessarily the best carriers for supported noble metal catalysts. Since the noble metal

component is responsible for exceptionally high activity at low temperatures, different mechanisms are occurring and dispersion characteristics, as well as interactions between the noble metal and carrier dictate overall catalyst performance. Carrier compositions that optimize these qualities do not necessarily have high inherent activity in the absence of noble metals.

Table 2 contains a summary of Pt-containing catalyst compositions for conversion of toluene and MEK to CO₂. The

first entry in the table shows that 5%Pt/MO1 also is very active at low temperatures for MEK destruction with 73% conversion at 80°C and 29% conversion at only 60°C. The 5%Pt/MO2 catalyst also consisted of Pt supported on a single-component metal oxide, and this composition demonstrated improved activity for toluene destruction with 49% at 80°C. Further improvements in performance for toluene destruction were achieved by washcoating 12 wt.% MO1 onto MO2 and using this combined metal oxide as a support for Pt. With only 0.8% Pt loading, this catalyst demonstrated nearly the same activity as 5%Pt/MO2. The greatest low-temperature activity for toluene destruction was 61% at 80°C using 5%Pt/MMO9, where MMO9 was a doped analog of MO1.

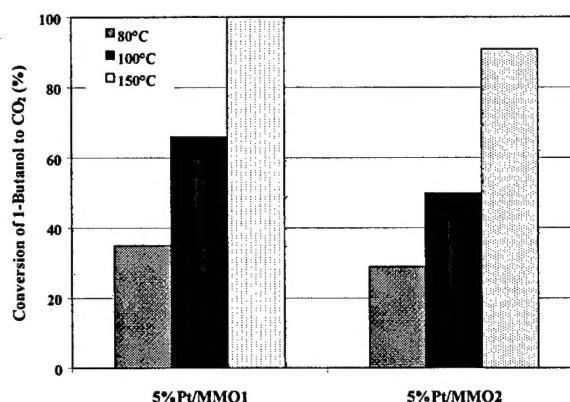


Figure 5. Summary of activity for conversion of 1-butanol to CO₂ at 80°C, 100°C, and 150°C for 5% Pt supported on the multi-component metal oxides MMO1 and MMO2. The 1-butanol concentration was ~100 ppm and the space velocity was ~6,000 hr⁻¹.

Table 2. Summary of supported-Pt catalysts for low-temperature conversion of toluene and MEK to CO₂.*

Catalyst	VOC	Conversion at 60°C (%)	Conversion at 80°C (%)
5%Pt/MO1	Toluene		37
	MEK	29	73
5%Pt/MO2	Toluene		49
0.8%Pt/12%MO1/MO2	Toluene	4	45
5%Pt/MMO9	Toluene	16	61
	MEK	22	39
5%Pt/MMO10	Toluene	2	26
	MEK	28	35
5%Pt/MMO11	MEK		35

*VOC concentration was ~100 ppm, and the space velocity was between ~1,000 and 6,000 hr⁻¹.

CONCLUSIONS

Catalysts tested in this work demonstrated high activity for low-temperature destruction of VOCs with a range of functional groups. Catalysts with the best overall performance in the absence of noble metals were multi-component metal oxides selectively derived from single-component analogs. Under practical conditions, these catalysts generated complete conversion of 1-butanol to CO₂ at 150°C, 47% conversion at 100°C, and 15% conversion at 80°C. For toluene, these catalysts generated complete conversion at 200°C, and as high as 75% conversion at 150°C. These results demonstrated that substantial improvements in oxidation activity of metal-oxide based materials can be achieved with relatively minor modifications in composition. Adding Pt to these materials further improved low-temperature activity and routinely enabled greater than 50% conversion of VOCs at temperatures of 100°C and lower. At the VOC concentrations, flow rates, and test temperatures used in this work, periods between 3 and 24 hours were required to establish steady-state conditions. It is likely that the source of this induction period was associated with adsorption of VOCs onto the catalyst surface. Although generally it was found that catalytic destruction decreased in the order of 1-butanol > MEK > toluene, some of the most active materials demonstrated different trends, as well as large disparities in activity for these VOCs. Therefore, actual application of these materials for treating mixtures of VOCs likely will require either a compromise in composition for best overall activity, or compositions will need to be selected to target a specific VOC. Finally, it was concluded that the multi-component metal oxides with the highest activity in the absence of noble metals were not necessarily the best carriers for supported-Pt catalysts.

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KEY WORDS

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